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Neutral aldoses derived from sequential acid hydrolysis of sediments as indicators of diagenesis over 120,000 years

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ABSTRACT

Neutral aldoses of the upper 50 m (representing ca. 120 kyr) of sediments from the Cariaco Basin were studied using a new technique based on water extraction followed by sequential acid hydrolysis with 2N, 4N and 6N trifluoroacetic acid (TFA) to investigate the fate of carbohydrates during diagenesis. The distribution and abundance of neutral aldoses and their evolution with depth shed light on the origin and fate of carbohydrates upon burial. The carbohydrates originated mainly from phytoplanktonic production, in particular diatoms. The porewater carbohydrate fraction was invariant and its composition attested to considerable biodegradation of the source material. Bacteria in the sediment may have also contributed to this fraction. The carbohydrates in the 2N fraction represented a decreasing fraction of the total organic carbon (TOC) with increasing depth/age. This fraction likely derived from storage polysaccharides, which were progressively degraded in the sediment. The 4N fraction was dominated by hexoses, suggesting that it comprised sugars derived from structural polysaccharides and exopolymeric substances. It showed a slight decrease with depth, over the 120 kyr. The 6N fraction comprised a relatively constant fraction of TOC with sediment depth. The aldose distribution suggested that the 6N fraction showed the imprint of the initial biological signal preserved by a proteinaceous macromolecular structure and/or a mineral matrix, but not from condensation in the sediment of more labile polysaccharides.

1. Introduction

Carbohydrates are important components of biomass, where they act as storage and structural compounds. They represent > 70 wt% of the total organic carbon (TOC) in vascular plants (Moers et al., 1993) and 20–40 wt% of plankton TOC (Parsons et al., 1984). Despite their abundance in marine organisms, they are often assumed to be only minor contributors to the TOC budget in sediments (Tissot and Welte, 1984). Nevertheless, during the last few decades, they have been the center of many studies to trace the sources and fate of organic matter (OM; Cowie and Hedges, 1984a; Kerhervé et al., 2002; Khodse et al., 2008).

Polysaccharides are rapidly degraded to monomers in shallow marine water (< 300 m; Pakulski and Benner, 1994) and at the oxic/anoxic interface in a stratified water column (Sass et al., 2001; Taylor et al., 2009). However, not all polysaccharides are degraded in the water column. For instance, carbohydrates associated with exopolymeric substances (EPSs) produced by plankton and bacteria can be exported to deeper water and sediments through the formation of aggregates (Verdugo et al., 2004). Some polysaccharides reach the anoxic layer of the sediment, where they are partially degraded by the specific exoenzymes excreted by benthic microbes. The latter use only simple substrates and short carbohydrates with a size limit of 600 Da (the size of a trisaccharide; Weiss et al., 1991; Arnosti and Holmer, 1999), leaving a complex mixture of incompletely degraded organic products (Cowie and Hedges, 1984a).

In recent marine sediments, acid-hydrolyzable sugars account for only 5–10% of the TOC (Burdige et al., 2000; Unger et al., 2005; Khodse et al., 2008). However, several studies indicate that the macromolecular OM (kerogen) of a large number of sedimentary rocks is composed mainly of condensation and polymerization products of sugars (Sinninghe Damsté et al., 1998; Riboulleau et al., 2000; van Dongen et al., 2006). This difference between the recovered intact sugars and those in macromolecular OM could lie in the techniques used for sugar extraction from recent sediments. In most studies, polysaccharides are hydrolyzed using low

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acid concentration (1.2 M H_2SO_4 or HCl) pre-treated with concentrated H_2SO_4 (Cowie and Hedges, 1984a). However, strong acid hydrolysis has been shown to produce unwanted reactions between sugars and amino acids (Allard et al., 1997), forming non-hydrolysable condensed structures (melanoidins) through the Maillard reaction (Maillard, 1912). Melanoidins have been observed in several kerogens from recent sediments (Zegouagh et al., 1999; Garcette-Lepecq et al., 2000; Aycard et al., 2003) but could have been formed during sample treatment. These artifacts are problematic for the interpretation of preservation pathways involved in the accumulation of sedimentary OM. However, their formation can be avoided by using sequential acid hydrolysis with trifluoroacetic acid (TFA; Allard et al., 1998). Moreover, since glycosidic bonds in polysaccharides and conjugated sugars (e.g. storage and structural polysaccharides, cellulose carbohydrates, EPSs and randomly condensed degradation products) react differently upon acid treatment, sequential hydrolysis with TFA allows recovery of sugars with different stability, providing information about the structure of the carbohydrate pool in the sediments. TFA treatment is also recommended because the acid can be easily removed due to its volatility (Fengel and Wegener, 1979; Amelung et al., 1996).

In the present study, OM-rich sediments from the Cariaco Basin, Venezuela, were treated with increasing acid strength and time of exposure to target different carbohydrate groups based on their resistance to acid hydrolysis. We hypothesized that carbohydrates in structural components would be more resistant to acid hydrolysis and would persist longer in sediments than carbohydrates used for energy storage. Carbohydrate diagenesis was tracked back through analysis of samples covering an interval of 120 kyr.

2. Methods

2.1. Study area

The Cariaco Basin, on the northwestern Venezuelan shelf, is the second largest anoxic–sulfidic marine basin after the Black Sea (Fig. 1a). It is isolated from the Caribbean Sea by a shallow sill restricting the renewal of bottom water and has experienced anoxic conditions for about 15 kyr (Peterson et al., 1991). Climate-induced fluctuation from oxic to anoxic conditions has occurred for the last 580 kyr (Peterson et al., 2000). The regional climate is controlled by the migration of the Inter-tropical Convergence Zone (ITCZ), which determines the alternation of dry and rainy seasons at an annual scale. Thus, during boreal winter, the ITCZ is at its southernmost position, inducing the development of trade winds along the Venezuelan coast and producing a seasonal upwelling recorded in sediments as a light colored carbonate and opal-rich biogenic lamination. Conversely, its northernmost position induces an increase in rainfall, which affects the surrounding riverine system, increasing the input of terrigenous material (Hughen et al., 1996). Similar variation is also observed on a millennial scale, with a southward migration of the ITCZ during cooler periods, e.g. the Younger Dryas, cold stadials of the last glacial and a northward migration during the warm interstadials and interglacial periods, e.g. the Holocene and Eemian (Peterson and Haug, 2006).

2.2. Sample collection

Samples (13) were collected from dark and laminated intervals and originated from three cores (Fig. 1b). The first 5 were obtained from a piston core (10°40′39″N, 64°58′14.5194″W; water depth 850 m) collected during the PICASSO (IMAGES XI) campaign of the RV Marion Dufresne in May 2003, covering the Holocene (Fig. 1). The other 8 were from cores collected from holes D and E on the central saddle of the Cariaco Basin during ODP Leg 165 at site 1002 (10°42.3660N, 65°10.1660W; water depth 873 m; Fig. 1a). The samples were collected from core depths ranging from 0.6–45 m, corresponding to ages in the range 2000–127,000 yr (Table 1).

According to a previous study (Riboulleau et al., 2011), the sediment in core MD03-2625 and hole ODP 1002 has identical TOC content and hydrogen index (HI) on the 0–14.7 kyr interval, despite the different locations in the basin. For this reason, we consider the OM at the two locations to be comparable and the composite record is considered as equivalent to a single core.

The age model for the cores is presented in detail by Riboulleau et al. (2014). Briefly, for core MD03-2625, the age model was determined by correlating the colorimetric parameter (a^*), describing sediment color in the range red to green (Laj and Shipboard Scientific Party, 2004), with gray scale data for core PL07-56PC using the age model of Hughen et al. (2000). The software used for the correlation was AnalySeries (Paillard et al., 1996). For holes ODP 1002D and E, the age model was established after correlation of the two cores based on pictures, sediment lightness (L^*) and magnetic susceptibility acquired on board (Shipboard Scientific Party, 1997), allowing establishment of a composite depth scale. Using the latter, the age model for the interval between 10 and 75 kyr was derived from the age model established by Hughen et al. (2006) for hole 1002D. Beyond 75 kyr, the age model was derived from that established by Drenzek (2007) for hole 1002D. Samples were composed of silty clay, with a variable proportion of diatoms, coccoliths, scattered foraminifers and pteropods.

2.3. TOC content

TOC content was obtained from Rock-Eval pyrolysis (Espitalié et al., 1985), performed on 100 mg aliquots of bulk sediment. Standard conditions for samples containing recent OM were used, i.e. 180 °C for 3 min initially, followed by programmed pyrolysis at 30 °C/min to 550 °C under He flow and then oxidation at 600 °C for 7 min under O_2 flow. Analyses were carried out at the Institut des Sciences de la Terre de Paris, Université Pierre et Marie Curie (Paris 6).

2.4. Neutral aldose concentration

Measurement of neutral aldose concentration was performed at the Unité de Glycobiologie Structurale et Fonctionnelle, Université Lille 1. To obtain the corresponding sugars, ca. 5 g desiccated sediment were treated sequentially to provide the water-soluble neutral aldoses and hydrolysable neutral aldoses.

2.4.1. Water-soluble neutral aldoses

The water-soluble aldoses (WSNAs) were obtained by extraction with 10 ml triple distilled water at room temperature for 5 min using a vortex mixer (5 × to a total of 50 ml). The supernatant was filtered using Sartorius sterile syringe filters (0.45 μm); 10 ml aliquots were lyophilized prior to hydrolysis using 4N TFA for 4 h at 100 °C.

2.4.2. Hydrolysable neutral aldoses

The hydrolysable neutral aldoses (HNAs) were obtained via successive hydrolysis of the desalted dry sediment using 25 ml TFA, permitting characterization of three fractions: (i) 2N TFA, 100 °C, 4 h; (ii) 4N TFA, 100 °C, 18 h; (iii) 6N TFA, 105 °C, 24 h. Between the water extraction and the acid treatment, the dry desalted sediment was extracted 2 × for 10 min using CH_2Cl_2/MeOH (2:1, v/v) in a Dionex ASE 200 accelerated solvent extractor at 50 °C and 80 bar. This extraction does not influence the neutral monosaccharide yield, as reported by Moers et al. (1990).